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MICROSTRUCTURE AND PROPERTIES OF HVOF-SPRAYED Ni-50Cr COATINGS

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ABSTRACT

Chromia-forming Ni-50%Cr coatings were prepared by a HVOF thermal spray process and characterized. The microstructure and physical and mechanical characteristics are similar to other metallic HVOF coatings recently studied: low fractions of porosity and oxide are observed combined with compressive residual stresses. The performance of Ni-50%Cr coatings in corrosion tests in simulated coal combustion gas and gas-slag environments was slightly worse than FeAl and Fe_3Al coatings prepared by similar processes. The corrosion behavior of the iron aluminide coatings was only slightly worse than a wrought Fe_3Al-based alloy.

INTRODUCTION

Advanced fossil energy systems, such as FutureGen and Vision 21, are being designed for high efficiency and low or zero emissions. Increased efficiency requires increased operating temperatures, whether steam temperatures for steam raising plants and combustion gas temperatures for gas turbines. Advanced fossil-fired steam plants also use higher steam pressures with final steam conditions into the ultrasupercritical regime of 30 MPa pressure and 600°C temperature[1]. These conditions require greater high-temperature strength from structural materials, e.g., tubing and piping, and have led to consideration of new alloy systems for these components, such as Fe-Al intermetallics and Ni-base alloys, instead of the more traditional ferritic steels.[2]

Higher operating temperatures also increase the kinetics of high-temperature corrosion processes, both fireside and steamside, a problem which is further exacerbated by altered operating conditions to produce lowered emissions (low NO_x burning).[3] For a given component corrosion conditions may range from oxidizing to reducing to sulfidizing to carburizing depending on the local environment, and erosion frequently contributes to the corrosive attack.[4] Existing and advanced materials which have been designed primarily with creep strength in mind may not possess adequate resistance to such aggressive environments.[3]

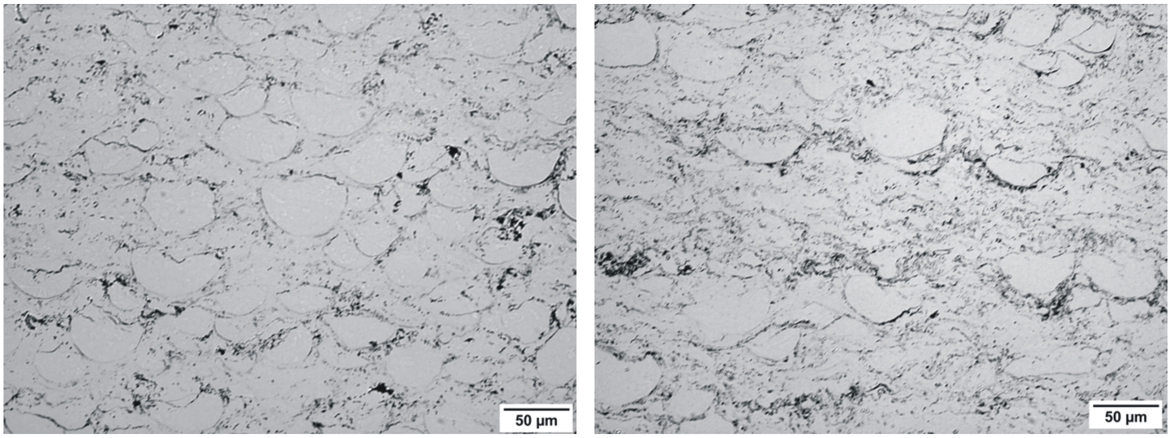
A solution to this problem is the use of coatings to provide or enhance the corrosion resistance of high-strength alloys. For example, high-temperature corrosion-resistant coatings are essential to the operation of advanced aerospace gas turbine engines. Materials used for coatings typically form very stable alumina, chromia, or silica layers and are applied in a variety of ways, including solid-state diffusion, chemical and physical vapor deposition, and thermal spraying. Of these, thermal spray techniques hold the most promise for large fossil energy systems due to their lower expense and potential for field application. Thermal spray coatings of many types currently find wide use in a number of industries for corrosion and wear protection.

The overall goal of Idaho National Laboratory research on thermal-spray coatings for high-temperature environmental resistance has been to better understand the relationships between coating processes, coating characteristics, and coating performance. Towards these ends, the effects of coating process variables (primarily thermal spray particle temperature and velocity) on the characteristics of alumina- and silica-forming coating materials have been studied. These include iron aluminides formed by high-velocity oxy-fuel (HVOF) spraying and Mo-Si-B coatings formed by air plasma spraying (APS).[5-7] This paper describes the preparation and characterization of chromia-forming Ni-50%Cr thermal spray coatings by the HVOF process. The Ni-50%Cr alloy composition is similar to that of the INCOCLAD 671 cladding which has shown excellent performance in the Niles service plant tests.[8] The corrosion resistance of iron aluminide and Ni-50Cr coatings was compared in simulated coal combustion gas and gas-slag environments at test temperatures ranging from 500 to 800°C. In both environments the iron aluminide coatings show superior corrosion resistance not markedly different than Fe_3Al in wrought form.

EXPERIMENTAL METHODS

PREPARATION AND CHARACTERISTICS OF Ni-50%Cr COATINGS

Ni-50wt.%Cr coatings 250 µm to 1500 µm thick were prepared from gas-atomized powder by HVOF thermal spraying in air onto Grade 91 steel and 316 stainless steel substrates. Coatings were produced at two different torch chamber pressures, 340 and 620 kPa, which resulted in varied mean spray particle velocities and temperatures. Coating microstructures were examined using standard techniques; residual stresses as a function of coating thickness were characterized by curvature measurements of coating-substrate couples using the Stoney approximation as described in Ref. [9]. Mean coefficients of thermal expansion (CTE) were measured on free-standing coatings using a vertical dilatometer. Tensile adhesion tests (ASTM C 633) were performed on coatings sprayed onto Grade 91 steel and 316 stainless steel substrates. Typical coating microstructures are shown in Figure 1; spray conditions and coating characteristics are listed in Tables 1 and 2. The microstructure and characteristics of the Ni-50%Cr coatings are similar to other metallic coatings prepared by HVOF thermal spray—porosity is low and residual stresses are compressive and increase with spray particle velocity.



(a) (b)

Figure 1: Microstructures of Ni-50%Cr coatings sprayed at (a) 490 m/s and (b) 540 m/s particle velocities.

Table 1: Ni-50%Cr coating spray conditions and microstructural characteristics

Spray conditions			Microstructural characteristics		
HVOF chamber pressure (kPa)	Mean spray particle velocity (m/s)	Mean spray particle temperature (°C)	Porosity (%)	Oxide (%)	Unmelted particles (%)
340	490	1480	0.05	5	28
620	540	1680	0.05	5	16

Table 2: Ni-50%Cr coating physical characteristics

Particle velocity (m/s)	Residual stress (MPa)	Microhardness (VHN)	Mean CTE @ 700°C (ppm/°C)	Tensile adhesion strength	
				Grade 91 substrate (MPa)	316 SS substrate (MPa)
490	– 100	440	15.3	6.2-7.0	4.8-6.2
540	– 400	500	14.6	7.4-9.0	4.8-5.9

TGA CORROSION TESTING

Corrosion tests were performed on free-standing iron aluminide and Ni-50%Cr coatings and a wrought Fe_3Al-based alloy. Fe_3Al and FeAl coatings were prepared by HVOF spraying onto stainless steel substrates at spray particle velocities of 560 and 620 m/s for Fe_3Al and 540 and 700 m/s for FeAl.[6, 7] Ni-50%Cr coatings were prepared at spray particle velocities of 490 and 540 m/s as described above. Coatings roughly 1.5 mm thick were created from which free-standing rectangular coating TGA specimens 4 × 4 × 0.5 mm^3 were machined. Similar-sized specimens were machined from wrought Fe_3Al sheet (alloy FAS with 2% Cr). Isothermal TGA tests were performed at 500, 600, 700, and 800°C for 25 hr and 100 hr durations in an environment of flowing (~200 ml/min) N_2-9%CO-4.5%CO_2-1.8%H_2O-0.12%H_2S. This is the mixed oxidizing-reducing environment used by Lehigh University[10] and Albany Research Center.[11] For this gas mixture the equilibrium oxygen and sulfur activities are reported as 10^{-19} and 10^{-8}, respectively. For all materials reaction rates typically decreased at the beginning of the tests, sometimes becoming linear at longer times. Consistent linear, parabolic, or paralinear behavior was not observed. For the purpose of material and temperature comparison the corrosion rates were characterized by a linear fit to the weight gain versus time curve near the end of the test.

GAS-SLAG CORROSION TESTING

A variety of free-standing thermal spray coatings were corrosion tested in a simulated coal combustion environment: the gas mixture given above and contact with iron sulfide powder to simulate furnace coal ash. The iron sulfide powder was contained on top of each specimen in a quartz ring. Grade 91 steel substrate material was tested for comparison. Specimens were isothermally exposed to the gas-slag environment for 100 hours at 700°C in a tube furnace and also to thermal cycling conditions which consisted of heating to 700°C, a 1 hour hold at 700°C, and furnace cooling to 100°C. This cycle was repeated 75 times such that the time specimens were held between 600 and 700°C was equal to 100 hours. The depth of corrosion was measured after exposure by metallographic evaluation: the tested specimens were potted in epoxy along with the iron sulfide powder and quartz ring, sectioned in half, and prepared for metallography.

RESULTS AND DISCUSSION

TGA CORROSION TESTING

Results of TGA tests of Ni-50%Cr coatings in simulated coal combustion gas are shown in Figure 2 in the form of weight gain versus time for individual tests at all temperatures. No consistent trends in rates of magnitudes of weight gain with temperature or spray particle velocity are present. Figure 3 further illustrates this point and compares data obtained on Ni-50%Cr coatings with those from iron aluminide coatings and wrought Fe_3Al reported previously.[12] The lack of consistent trends in data between the different coating materials is clear, but wrought Fe_3Al does appear to show slightly better performance than the coatings. The reason for the lack of trends is currently unclear; it is suspected that the environment is not sufficiently aggressive to clearly differentiate the materials, since the low weight gains observed correspond to little observable corrosion (about one micron of attack)., and variable initial weight gains may be overwhelming the true behavior.

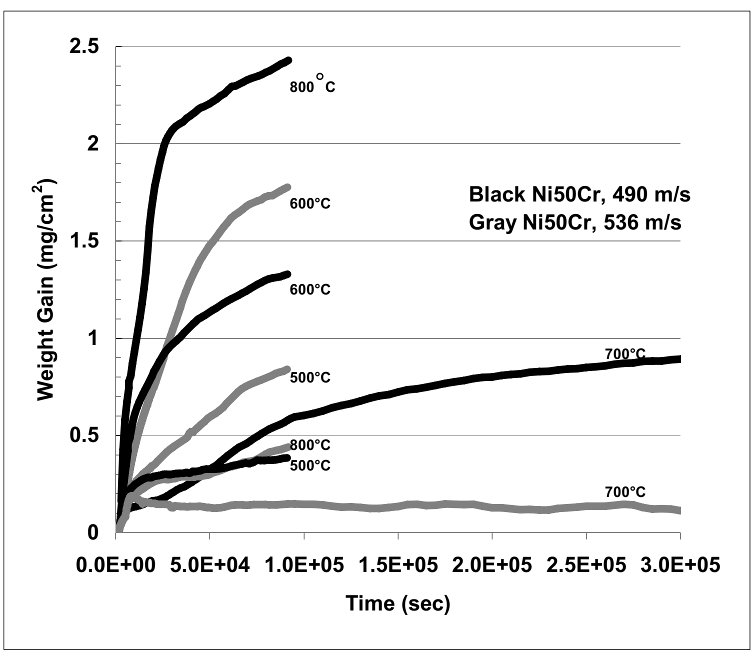


Figure 2: Weight gain versus time for free-standing Ni-50%Cr coatings in a simulated coal combustion gas environment.

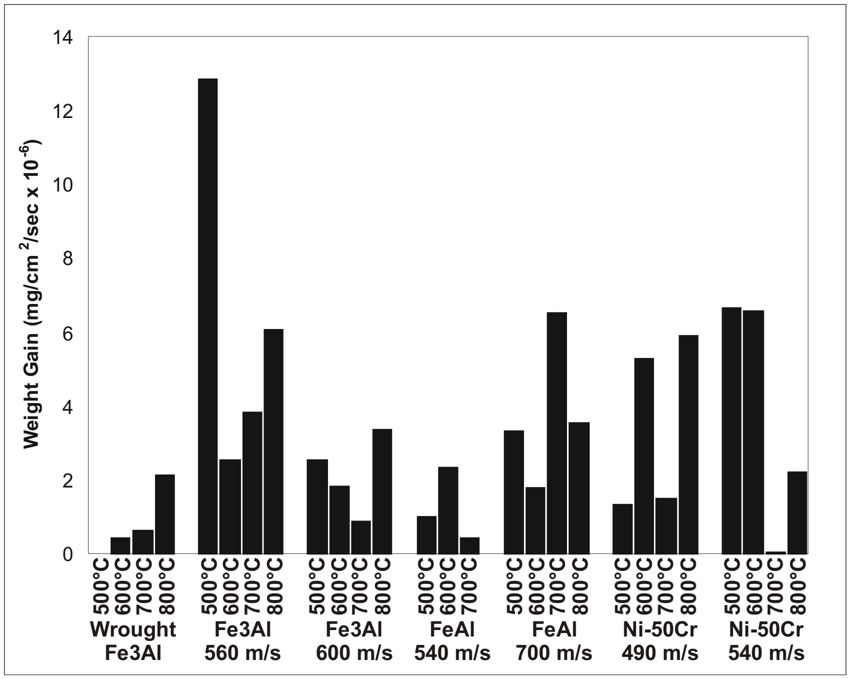


Figure 3: Comparison of linear weight gain rates in simulated coal combustion gas environment for different coating materials and temperatures.

GAS-SLAG CORROSION TESTING

SEM micrographs of typical corrosion layers for the different materials tested in the gas-slag environment are shown in Figures 4 through 7; Table 3 lists approximate average depths of attack. The iron aluminides were the most resistant; the behavior of wrought Fe_3Al and FeAl coatings was comparable. Fe_3Al and Ni-50%Cr coatings showed more attack. The Grade 91 steel was severely attacked in the isothermal test, much less so in the cyclic test; the reason for this is unknown. Corrosion depths were generally greater in the isothermal exposure, contrary to the expected accelerating effect of thermal cycling. A possible explanation for this effect is that the exposure duration in the cyclic tests was not equivalent to 100 hours. Only 75 one-hour hold periods were performed, and the additional time at temperatures near 700°C during heatup and cooldown may not have significantly contributed to the corrosion process, contrary to expectations. There was no significant effect of spray particle velocity in the FeAl and Ni-50%Cr coatings, but greater corrosion was observed for the Fe_3Al coating sprayed at the higher velocity.

Given the generally good corrosion resistance shown by the coatings in this series of tests, future work will focus on mechanical aspects of coating failure, i.e. adhesion and cracking resistance.

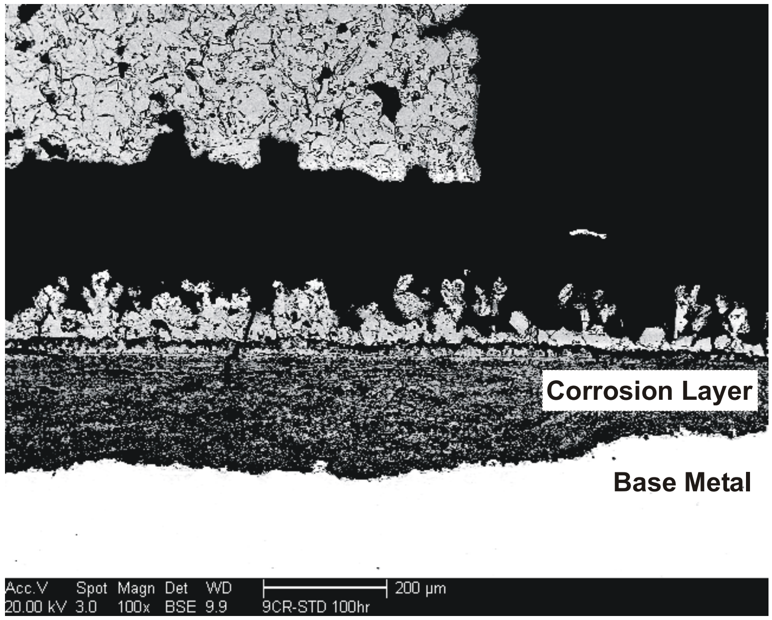


Figure 4: Typical corrosion layer observed in Grade 91 steel exposed to iron sulfide and simulated coal combustion gas at 700°C for 100 h (100X).

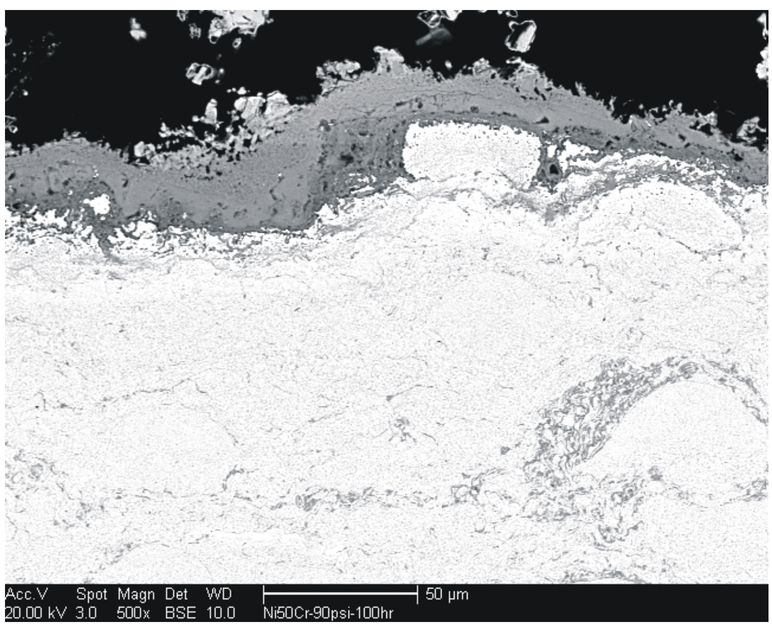


Figure 5: Typical corrosion layer observed in Ni-50%Cr coating sprayed at 540 m/s, exposed to iron sulfide and simulated coal combustion gas at 700°C for 100 h (500X).

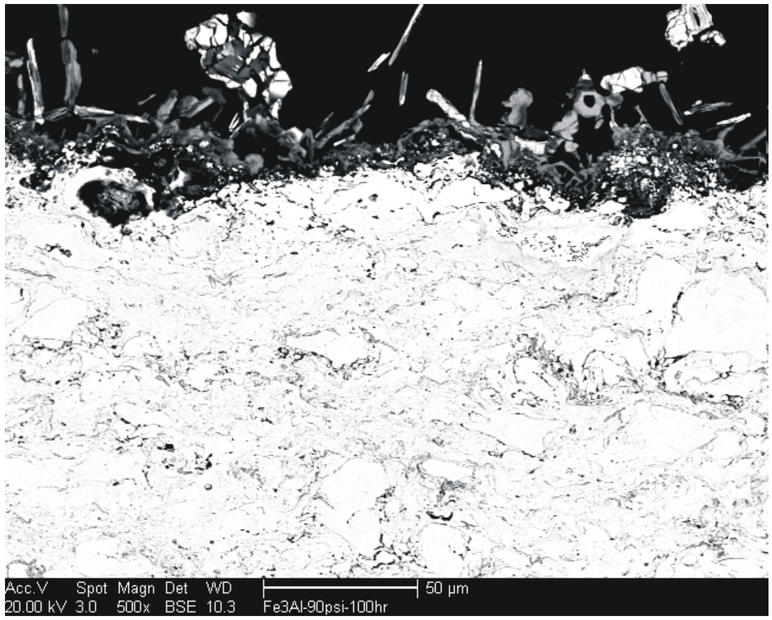


Figure 6: Typical corrosion layer observed in Fe_3Al coating sprayed at 620 m/s, exposed to iron sulfide and simulated coal combustion gas at 700°C for 100 h (500X).

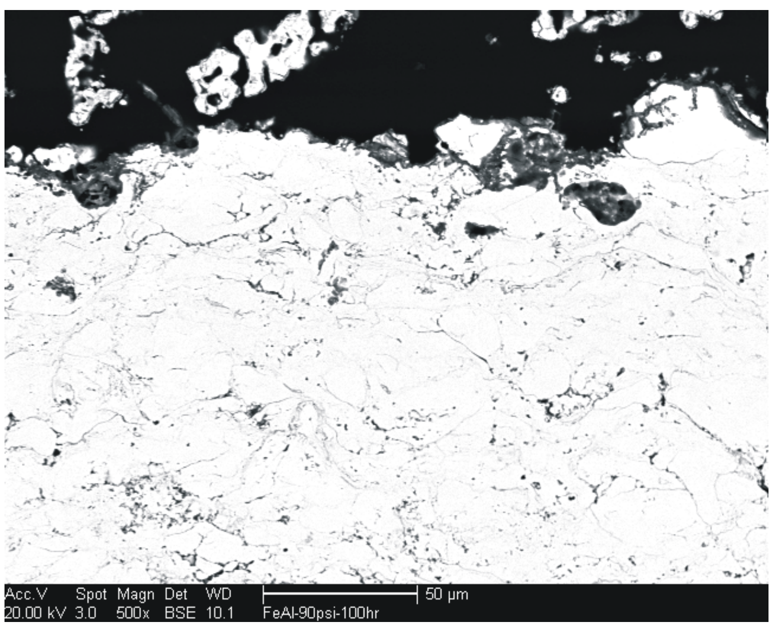


Figure 7: Typical corrosion layer observed in FeAl coating sprayed at 700 m/s, exposed to iron sulfide and simulated coal combustion gas at 700°C for 100 h (500X).

Table 3: Average corrosion depths observed in gas-slag corrosion tests

Material	Isothermal corrosion depth (μm)	Cyclic corrosion depth (μm)
Ni-50%Cr coating, 490 m/s	24	26
Ni-50%Cr coating, 540 m/s	27	20
FeAl coating, 540 m/s	3	3
FeAl coating, 700 m/s	4	1
Fe_3Al coating, 560 m/s	8	6
Fe_3Al coating, 620 m/s	20	11
Wrought Fe_3Al	5	1
Grade 91 steel	210	24

CONCLUSIONS

Chromia-forming Ni-50%Cr coatings were prepared by a HVOF thermal spray process and characterized. The microstructure and physical and mechanical characteristics are similar to other metallic HVOF coatings recently studied: low fractions of porosity and oxide are observed combined with compressive residual stresses. The performance of Ni-50%Cr coatings in corrosion tests in simulated coal combustion gas and gas-slag environments was slightly worse than FeAl and Fe_3Al coatings prepared by similar processes. The corrosion behavior of the iron aluminide coatings was only slightly worse than a wrought Fe_3Al-based alloy.

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